

**Key Words:** Plutonium, oxidation state, pH, soil, sediment

**Retention:**  
**Permanent**

## **Influence of pH and Oxidation State on Plutonium Mobility Through an SRS Sediment**

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**October 28, 2001**

Westinghouse Savannah River Company  
Savannah River Site  
Aiken, SC 29808



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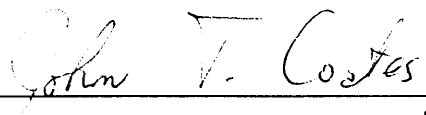


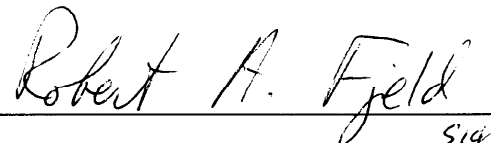
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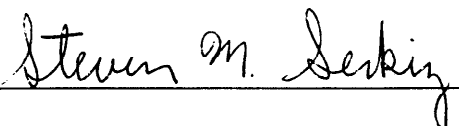
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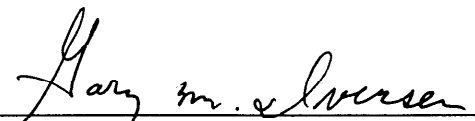
## REVIEWS AND APPROVALS


  
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## 1.0 EXECUTIVE SUMMARY

The environmental mobility of Pu is profoundly influenced by its oxidation state. Pu(IV) is 2 to 3 orders of magnitude slower moving than Pu(V) or Pu(VI). For performance and risk assessment calculations, Pu waste has been assumed to exist in the less mobile reduced form, Pu(IV). Recent work on the chemistry of PuO<sub>2</sub> by Haschke and others has shown that PuO<sub>2</sub> is not the thermodynamically stable form as had previously been understood. Rather, some of the PuO<sub>2</sub> surface is oxidized in the presence of water, forming as much as 27% Pu(VI). This has significant implications to existing SRS programs (including the Pu Immobilization, LLW Disposal, and Remediation of the Old Burial Ground) and future SRS programs (including MOX and pit disassembly). Aspects of these implications are captured in the SRS Technology Needs/Opportunity Statement SR00-1026, "Reduce the Conservatism and Technical Uncertainty Associated with the Use of Literature Coefficients ( $K_d$ ) to Describe Radionuclide Sorption to Sediments in PA Modeling."

The hypothesis of this Strategic Research and Development study is that even if Pu(VI) is produced as suggested by Haschke and others, it will be quickly reduced to Pu(IV) in the SRS subsurface environment. The overall objective of the study research is to test this hypothesis and provide definitive data on the oxidation state of Pu at the site.

This project was initiated in February of this year. This report includes two journal manuscripts describing the work completed to date. Both manuscripts have been submitted for internal release (for STI approval). The first paper describes laboratory experimental work and is entitled "Influence of pH and Plutonium Transport Through a Coastal Plain Soil in a Low Carbonate Environment." It will be submitted to Environmental Science and Technology. The second manuscript describes the reactive transport modeling results of the laboratory data presented in the first manuscript and is entitled, "Evaluation of a Conceptual Model for the Subsurface Transport of Plutonium Involving Surface Mediated Reduction of Pu(V) to Pu(IV)." It will be submitted to the Journal of Contaminant Hydrology.

In addition to this work providing SRS with much-needed information regarding plutonium geochemistry at the site, it also permitted our group to develop new laboratory and reactive transport modeling skills. We intend to include aspects of this data in a proposal to the forthcoming Environmental Management Science Program (EMSP – DOE) request for proposals.

Below are the abstracts to each manuscript.

Influence of pH and Plutonium Transport Through a Coastal Plain Soil in a Low Carbonate Environment: Laboratory-scale studies were conducted on a coastal plain soil from the U. S. Department of Energy's Savannah River Site (SRS) to evaluate the influence of solution pH, redox state, and speciation on the transport of plutonium (Pu). Both batch and column approaches were used to study the influence of pH (3, 5, and 8) on the sorption and transport of Pu(V). Over the almost three-day test period, Pu(V) batch sorption kinetics showed continual

removal of Pu from solution. This suggests the formation of a more strongly sorbing Pu specie(s) with time and is consistent with the formation of Pu(IV) by reduction of Pu(V). The effluent data for the column tests show the presence of multiple Pu species. The breakthrough curves were all characterized by a well-defined peak in which the mean retardation factor,  $R$ , and the fractional breakthrough varied with pH. The mean breakthrough fractions and  $R$  values of the major Pu peak at pH 3, 5, and 8 were 0.90 at  $R = 1.4$ , 0.75 at  $R = 8.4$ , and 0.38 at  $R = 35$ , respectively. After the passage of the major peak, analysis of the sediment showed Pu distributions also with a wide range of mobilities. Although the system tested is chemically and hydrologically relatively simple, there are a number of processes that could be important including colloidal transport, aqueous-phase speciation changes, and solid-phase speciation changes. Filtration ( $<0.02\text{-}\mu\text{m}$ ) analysis suggests that the multiple Pu peaks in the breakthrough curves were not attributable to the presence of colloidal and non-colloidal phases. Oxidation state analyses showed the Pu in the major effluent peaks to be Pu(V) (at least for pH 3 and pH 5), it is likely that the first effluent peak is the  $\text{Pu(V)O}_2^+$  cation undergoing exchange reactions with the soil surface. Due to detection limit constraints, no oxidation state analyses are available on the less mobile low-activity peaks to discern their oxidation state distribution.

Evaluation of a Conceptual Model for the Subsurface Transport of Plutonium Involving Surface Mediated Reduction of Pu(V) to Pu(IV): A conceptual model is proposed to explain the transport behavior of plutonium in laboratory columns packed with a sandy coastal soil from the U. S Department of Energy's Savannah River Site. The column transport experiments, which are described elsewhere, involved the introduction of a finite step input of plutonium, predominately in the +5 oxidation state, into the columns and elution of the spike with a low-carbonate solution of 0.02 M  $\text{NaClO}_4$  at pH 3, 5, and 8. Total plutonium concentrations were measured in the effluent as a function of time. These elution profiles suggest at least two distinct physical/chemical forms of plutonium, each with a different mobility. To explain the observed behavior, a conceptual model is proposed here which includes [1] equilibrium partitioning (both sorption and desorption) of plutonium (V) and plutonium (IV) between the aqueous and sorbed phases with pH-dependent, oxidation-state specific distribution coefficients and [2] kinetic reduction of plutonium (V) to plutonium (IV) in the sorbed phase. The conceptual model was applied to the column experiments through a one-dimensional advective/dispersive mathematical model, and predictions of the mathematical model were compared with the experimental data. Overall, the model provided excellent qualitative predictions of the major features observed in the experiment. It also yielded a quantitative estimate of the rate constant for surface mediated reduction of plutonium (V) to plutonium (IV) that was in the range of values reported in the literature for goethite mediated plutonium reduction.

## 2.0 INFLUENCE OF pH AND OXIDATION STATE ON PLUTONIUM TRANSPORT THROUGH A COASTAL-PLAIN SOIL IN A LOW CARBONATE ENVIRONMENT

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### 2.1 ABSTRACT

Laboratory-scale studies were conducted on a coastal plain soil from the U. S. Department of Energy's Savannah River Site (SRS) to evaluate the influence of solution pH, redox state, and speciation on the transport of plutonium (Pu). Both batch and column approaches were used to study the influence of pH (3, 5, and 8) on the sorption and transport of Pu(V). Over the almost three-day test period, Pu(V) batch sorption kinetics showed continual removal of Pu from solution. This suggests the formation of a more strongly sorbing Pu specie(s) with time and is consistent with the formation of Pu(IV) by reduction of Pu(V). The effluent data for the column tests show the presence of multiple Pu species. The breakthrough curves were all characterized by a well defined peak in which the mean retardation factor, R, and the fractional breakthrough varied with pH. The mean breakthrough fractions and R values of the major Pu peak at pH 3, 5, and 8 were 0.90 at R = 1.4, 0.75 at R=8.4, and 0.38 at R = 35, respectively. After the passage of the major peak, analysis of the sediment showed Pu distributions also with a wide range of mobilities. Although the system tested is chemically and hydrologically relatively simple, there are a number of processes that could be important including colloidal transport, aqueous-phase speciation changes, and solid-phase speciation changes. Filtration (<0.02- $\mu$ m) analysis suggests that the multiple Pu peaks in the breakthrough curves were not attributable to the presence of colloidal and non-colloidal phases. Oxidation state analyses showed the Pu in the major effluent peaks to be Pu(V) (at least for pH 3 and pH 5), it is likely that the first effluent peak is the Pu(V)O<sub>2</sub><sup>+</sup> cation undergoing exchange reactions with the soil surface. Due to detection limit constraints, no oxidation state analyses are available on the less mobile low-activity peaks to discern their oxidation state distribution.

### 2.2 INTRODUCTION

Portions of the subsurface at the U. S. Department of Energy's Savannah River Site are contaminated with plutonium as a result of the historical disposal of wastes from nuclear materials processing. Laboratory investigations have shown that Pu sorption in this environment is highly variable (from a K<sub>d</sub> < 10 mL/g to > 10,000 mL/g (Prout, 1958)) and depends to a large degree on the groundwater pH, redox state of the Pu, the presence of complexants (e.g., carbonate and humic acids), formation of or association with colloidal material, and soil characteristics. Stated another way, the variability in Pu transport can be attributed to its complicated chemistry in natural systems.



Pu can exist in five oxidation states in aqueous solutions that include Pu (III), Pu (IV), Pu (V), Pu (VI), and Pu (VII). The chemical forms of these oxidation states essentially always occur as the hydrated ions of  $\text{Pu}^{+3}$ ,  $\text{Pu}^{+4}$ ,  $\text{PuO}_2^+$ ,  $\text{PuO}_2^{+2}$ , and  $\text{PuO}_5^{-1}$ , and studies have shown that multiple oxidation states can exist in the same solution (Cleveland, 1979). In natural systems Choppin et al. (1997) indicate that Pu(V) should be the dominant oxidation state in solution. Furthermore, hydrolysis reactions of Pu (IV) can lead to the formation of colloidal material of  $\text{Pu(OH)}_x$  which loses water to produce  $\text{PuO}_2$  (Cleveland 1979). In addition to these so-called intrinsic colloids, under certain specific conditions Pu has been shown to bind strongly to natural aquifer colloids (Kaplan et al., 1994) and these “associated colloids” have been implicated in facilitated transport of Pu at other nuclear sites (Kersting, 1999).

Pu chemistry in the solid phase is no less complicated and has been the subject of much recent research. A recent study of  $\text{Pu(IV)O}_2$  (s) exposed to water laden air by Haschke et al. (2000) has shown that this Pu(IV) solid does not exhibit the thermodynamic stability that had previously been accepted. Rather, in the presence of water, some of the plutonium surface had oxidized to the generally more mobile Pu (VI) with the evolution of hydrogen and the formation of  $\text{PuO}_{2+x}$  where x can range up to 0.27. In addition to the nature of the Pu-bearing waste affecting Pu transport, reactive surface coatings on soil particles have been shown to affect the groundwater transport of Pu. Sediment redox potential (which can be represented as Eh) has a profound influence on the tendency of plutonium to sorb to sediments. A number of investigators have examined potential sorption of plutonium on minerals, soils, and other geological substrates. The importance of plutonium redox status on sorption was demonstrated by Bondietti et al. (1975) who reported about 2 orders-of-magnitude difference in Kd values with montmorillonite between Pu (VI) (250 mL/g) and Pu (IV) (21,000 mL/g). Once in the subsurface environment, there are many naturally occurring materials that can cause the valence state of plutonium to change. Natural dissolved organic matter carbon (DOC) (e.g., fulvic and humic acids) has been shown to reduce plutonium from the +6 state to the +4 state (Bondietti et al., 1975; Nelson et al., 1987; Choppin and Morse, 1987). Similarly, naturally occurring Fe-oxides have been reported to reduce plutonium from the +5/+6 state to the +4 oxidation state in what is possibly an irreversible reaction (Sanchez et al., 1985; Keeney-Kennicutt and Morse, 1985). Conversely, Mn-oxides have been shown to potentially oxidize plutonium from the +4/+5 state to the +6 state (Duff et al., 1999).

Although the field data are sparse and subject to interpretation, the general complexity of Pu transport discussed above for laboratory studies is also observed for field studies. For example, Buddemeier and Hunt (1988) and Kersting et al. (1999) suggest the possibility that some fraction of plutonium can exhibit a higher than expected mobility in the subsurface. This has also been noted in several laboratory column studies (Fried et al., 1976; Thompson, 1989; Fjeld et al., 2001). Fjeld et al. (2001) observed three or more forms of plutonium, each with different mobilities, in sedimentary interbed from the Snake River Plain. The identification of the mechanisms that are responsible for high mobility transport is difficult because there are a number of hydrological and geochemical processes, either singly or in combination, that may strongly affect Pu mobility (e.g., aqueous phase speciation, quantity and character of surface sorption sites, and the presence of colloidal materials). Presented here are results of experiments

designed to elucidate the effect of pH on plutonium transport through columns containing a sandy coastal soil from the Savannah River Site.

## 2.3 MATERIAL AND METHODS

Generally, two separate soil-Pu(V) sorption studies were conducted over a range of pH conditions. The first employed a batch approach to investigate Pu(V) sorption kinetics and the second used a column approach to investigate Pu(V) transport. All solutions were prepared from reagent grade chemicals using DI water in acid-washed, double-rinsed glassware, unless otherwise specified.

### 2.3.1 Plutonium Solutions

The plutonium spike solutions were prepared with the low-carbonate 0.02 M NaClO<sub>4</sub> solution. Plutonium activities in the spike solutions ranged from 3.0 to 4.2 Bq/mL of <sup>238</sup>Pu (~2E-11M). The method of Saito et al. (1985) was used to prepare plutonium in predominantly the +5 oxidation state. Pu(V) has a relatively high solubility and a low tendency to undergo complexation reactions with carbonate (Choppin and Stout, 1989). Thermodynamic speciation modeling of Pu in the influent water was conducted using MinteqA2 (Allison et al., 1991) with the EQ3/6 aqueous stability constants and predicts that the dominant aqueous Pu(V) specie at pH values of 3, 5, and 8 will be Pu(V)O<sub>2</sub><sup>+</sup>. The aqueous speciation for Pu(IV) is more complicated with thermodynamic modeling predicting that about equal amounts of Pu(IV)(OH)<sub>2</sub><sup>2+</sup> and Pu(IV)(OH)<sub>3</sub><sup>+</sup> will be present at pH 3; Pu(IV)(OH)<sub>4</sub><sup>0</sup> will be the dominant specie at pH 5; and Pu(IV)(OH)<sub>5</sub><sup>-</sup> will be the dominant specie at pH 8. Furthermore, speciation modeling predicts that both Pu(IV) and Pu(V) should not be solubility limited at 2E-11M based on equilibrium with their respective hydroxide solids.

### 2.3.2 Soil

Experiments were performed with the 250 – 420 μm size fraction of a coastal sandy soil from the SRS. The whole soil was characterized by Johnson (1995) and was texturally classified as a sandy loam with kaolinite as the major clay mineral. This characterization showed the large amounts of extractable amorphous iron and aluminum which indicates the presence of reactive surface coatings of hydrous ferric oxide (HFO) and aluminum hydroxide (Table 1). Additionally, the specific surface area of the whole soil and the 250-420 μm size fraction were determined by BET nitrogen adsorption (Table 1).

Table 1. Soil Physical Properties<sup>(a)</sup>

pH in Water	% Sand	% Silt	% Clay	BET Surface Area, Whole Soil (m <sup>2</sup> /g)	BET Surface Area, 250-420 µm Fraction (m <sup>2</sup> /g)	Extractable Al (mg/kg)	Extractable Fe (mg/kg)
4.87	96.1	0	3.8	22.5	12.4	70	430

<sup>(a)</sup> All data are for whole soil except BET surface area for the 250-420 µm fraction. Column and batch studies were conducted with the 250-420 µm soil fraction.

### 2.3.3 Batch Sorption Kinetics Study

Batch sorption experiments were conducted to investigate the sorption of Pu(V) on the study soil. Low-carbonate 0.02M NaClO<sub>4</sub> Pu solutions were prepared at pH values of 3, 5, and 8. The Pu [predominantly as Pu(V)] activities in these solutions ranged from 4.2 to 4.4 Bq/mL (2.8E-11M). In a glove bag purged with low-carbonate air, 3.0 mL of the Pu solution were mixed with 3.0 g of the prepared soil in centrifuge vials. The centrifuge vials were capped and the vials were tumbled, outside the glove bag, for specified time periods of up to 4000 minutes (approximately 3 days). After reaction, solids were separated by centrifugation for 20 minutes at 3200 rpm. The aqueous phase was analyzed for Pu activity by liquid scintillation counting and the sorbed activity calculated from the difference in initial spike activity and the final activity.

### 2.3.4 Column Study

The column study apparatus consisted of reservoirs for the influents and the Pu spike solutions, a peristaltic pump (Masterflex, Model 7550-90), the column containing the soil, and a fraction collector (Eldex Universal Fraction Collector). Separate column tests were performed with influent water at pH 3, 5, and 8. The column dimensions were based on the methodology of Relyea (1982) for minimum flow velocities and column dimensions. The columns were constructed of polyvinylchloride cylinders with an inner diameter of 1.5 cm and a length of 8.7 cm. The columns were dry packed with the 250 – 420 µm size fraction of soil 0.5 cm at a time and compacted by lightly tapping the column on the benchtop. The porosity of the packed columns ranged from 0.30 to 0.34 and the bulk soil densities ranged from 1.62 to 1.66 g/cm<sup>3</sup>.

For the column study there were three pH influent treatments: pH 3, 5, and 8. A stock of low carbonate, 0.02 M NaClO<sub>4</sub> solution was prepared for all of the tests. NaClO<sub>4</sub> was chosen as the backing electrolyte because perchlorate has a very small stability constant for formation of complexes with Pu (Polzer and Miner, 1982). The stock solution was prepared by first boiling a 5.5 L volume of deionized water for 30 minutes to drive off dissolved gases. The remaining water was quickly transferred to a carboy equipped with a filling/venting cap. As the carboy was being cooled in cold water bath, low-CO<sub>2</sub> (<5 ppmv) air was bubbled through the water. The pressure of the low-CO<sub>2</sub> air was maintained high enough to ensure that the gas flow was from the carboy headspace to the atmosphere. After cooling, the filling/venting cap was sealed.

All subsequent transfers or sampling of these low-carbonate solutions were conducted in a glove bag (Instruments for Research and Industry, Model X-27-27) filled with the low-CO<sub>2</sub> air. The headspaces of all low-carbonate solutions were periodically purged with low-CO<sub>2</sub> air to ensure that CO<sub>2</sub> was being excluded. The acids and bases used for pH adjustment of the influent solutions were prepared using low-carbonate deionized water and were isolated in a glove bag during transfer.

During the column study, influent was passed upward through the column at a flow rate of 0.3 mL/min in the following order: (1) approximately one-half the soil column of the soil was wetted with pH adjusted low-carbonate 0.02 M NaClO<sub>4</sub> influent; (2) ~1 pore volume of a Pu/tritium spike solution was introduced ; and (3) column eluted with between 11 and 661 pore volumes of pH adjusted low-carbonate 0.02 M NaClO<sub>4</sub> influent. The effluent was collected in either 1.2 mL or 5.7 mL fractions. Long-term and a short-term tests were conducted with the above described procedure at each of the three influent pH values. One long-term test at each influent pH was conducted and subsequently terminated after 400 – 600 pore volumes. A second short-term test was conducted at each influent pH and terminated after the passage of the first Pu peak in the effluent.

### 2.3.5 Analyses

Analyses of the aqueous fractions were performed on 1-mL samples with an alpha/beta discriminating liquid scintillation counter (Wallac Inc., Model 1415), which is capable of determining <sup>3</sup>H and <sup>238</sup>Pu activities simultaneously (Ince 1996). Oxidation state analyses were performed on selected effluent aliquots of the short-term tests.

On selected aliquots from each of the short-term column tests, samples were filtered through disposable filters of 0.45, 0.20, and 0.02 μm nominal pore diameter and the resulting filtrate analyzed by liquid scintillation counting. Pu oxidation state analyses were performed using an extraction technique adapted from the thenoyltrifluoroacetone (TTA) / di(2-ethylhexyl) orthophosphoric acid (HDEHP) extraction technique discussed by Neu et al. 1994. Oxidation state analyses were also performed on the Pu spike solutions before the column tests. Major ion chemistry column tests were conducted at pH 3, 5, and 8 in the absence of Pu. The pH in the effluent was measured using a 50-μL micro-flow through pH sensor (Broadley-James Corporation) and a pH meter (VWR Scientific, Model 2000).

Following termination of the short-term tests, the soil columns were divided into nine segments. The two end segments were approximately 0.85 cm in length and the other seven segments were approximately 1-cm in length. Each segment was washed for 12 to 14 days in a solution containing 3 mL of 5 N HNO<sub>3</sub> and 3 mL of 5 N HCl. One-mL aliquots of the acid leaching solution were counted by liquid scintillation. The total aqueous volume in each vial was estimated gravimetrically so that the total Pu activity associated with each column segment could be estimated.

### 2.3.6 Data Analysis

The aqueous activities in the column effluent,  $C(t)$ , were normalized to the activity in the spike,  $C(0)$ , and plotted as a function of time, expressed as displaced pore volumes (DPV). Mean retardation factors for both  $^3\text{H}$  and the Pu fraction appearing in the effluent were determined using an adaptation of Clark's mean residence time determination approach (Clark, 1996). For the purpose of estimating retardation factors, the test was considered to be complete after the concentration of the eluted radionuclide no longer differed significantly from background.

## 2.4 RESULTS AND DISCUSSION

### 2.4.1 Batch Sorption Kinetics Study

Presented in Figure 1 are time-dependent distribution coefficients obtained from the batch experiments. Relative to other f-element sorption experiments conducted on this soil (Clark et al., 1998) where equilibrium was reached on the order of one-half a day, these data indicate that Pu(V) sorption equilibrium was clearly not reached even after almost three days. Further, there is a clear trend of increasing sorption as a function of increasing equilibration time that is consistent with the formation of a stronger sorbing Pu specie (e.g., reduction of Pu(V) to stronger sorbing Pu(IV)) during the batch sorption experiments. The pH trend for Pu sorption to the solid phase (i.e.,  $\text{pH}8 > \text{pH}5 > \text{pH}3$ ) is consistent with results of others (Mahara and Matsuzuru, 1989 and Sanchez et al., 1985) and follows the classic pH-dependence for the sorption of metal cations to metal oxide surfaces. Because equilibrium is not reached in 4000 minutes, about three days, it is unlikely that the Pu sorption in the column tests, where the residence time was 18 minutes, reached equilibrium conditions.

### 2.4.2 Column Study

Plutonium breakthrough curves and the solid-phase activity distribution at the end of the short-term tests are presented in Figures 2, 3, and 4 for the pH 3, 5, and 8 tests, respectively. The effluent activity profile at each pH is characterized by a major peak containing a large fraction of the Pu in the initial spike. Both the location of this major peak and the fractional breakthrough varied with pH (Table 2). With increasing pH, the mean fractional breakthrough decreased ( $f = 0.90, 0.75$ , and  $0.38$  at pH 3, 5, and 8, respectively) and the mean retardation factors increased ( $R = 1.4, 8.4$ , and  $35$  at pH 3, 5, and 8, respectively). At lower pH values, Pu transport is more rapid because the more positively charged soil surface results in lower cation affinity. As the influent pH increases, the soil becomes less positively charged and, all other factors being equal, cation sorption increases.

In all cases, a less defined and lower activity peak followed the first major peak. These peaks contained between 9 and 4 percent of the total Pu spike and decreased systematically with increasing pH. Because these peaks, especially at higher pH values, are not well defined, the Pu recovery in this second peak is to some degree determined by the test duration. Additionally, a

small but statistically significant quantity of Pu ( $<0.002$  of the Pu spike) eluted from the pH 8 columns between 1 and 2 DPV. Similar behavior has been observed by Fjeld et al. (2001) in column tests utilizing soils from the Department of Energy's Idaho National Engineering and Environmental Laboratory.

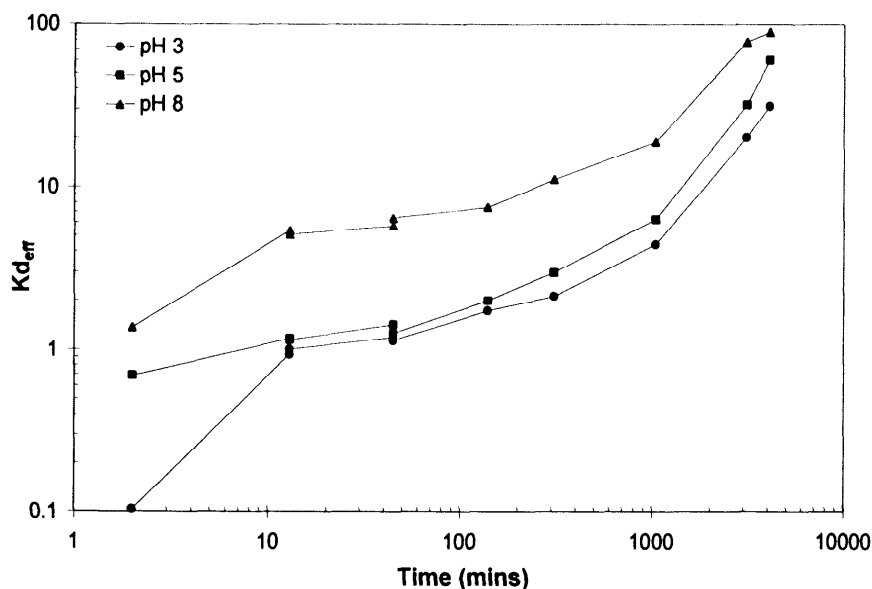


Figure 1. Pu Batch Sorption Kinetics.

Oxidation state analyses were performed on all of the spike solutions and on fractions from the peaks that appeared in the effluent in the short-term tests. The results (Table 3) confirm that the majority of the Pu in the spike solutions ( $\sim 90\%$ ) was in the Pu(V) state. The variability seen in the data is likely due as much to variability in the analysis technique as to actual oxidation state variability among the samples. The Pu(V) abundance in the effluent samples for the pH 3 and pH 5 tests did not differ substantially from that in the spikes. For pH 8, the Pu activity was too low for the analysis to be conducted. While the aqueous oxidation state results may appear to suggest that little or no reduction of the Pu(V) is occurring in the column, the notable variation in fractional recoveries of Pu as a function of pH necessitates that some change in the chemical form, either aqueous or surface, is occurring. If an ion-exchange model for this system were assumed to be an accurate representation of Pu sorption in this system, then the major change expected as a result of increasing pH would be a delay in the appearance of the effluent peak, but not a change in the mass of Pu contained in the peak. This Pu breakthrough behavior was not observed in our study. Instead, not only were the peaks delayed with increased pH, but the mass of Pu contained in the peak was reduced (Table 2), indicating that some other process(es) in addition to cation exchange was occurring in the columns. Furthermore, thermodynamic speciation modeling predicted that aqueous Pu(V) should exist as  $\text{PuO}_2\text{OH}^+$  at pH 3, 5, and 8 and, therefore, the multiple peaks were likely not attributed to different complexed aqueous

species of Pu(V). It is thought, therefore, that some change in sorbed Pu speciation is the most plausible mechanism for describing the observed data.

Table 2. Summary of Plutonium Transport Results

Influent pH	Average Effluent pH	Test Duration (DPV)	Integration Interval (DPV)	Mean Retardation Factor	Pu Recovery (%)		
					Effluent	Soil	Total
3	3.25	Long (452)	0 – 12	1.5	90	NA	
			12 – 452		9	NA	
5	4.90	Short (12)	0 – 12	1.3	90	12	102
		Long (660)	0 – 60	8.8	74	NA	
			60 – 660		8	NA	92
		Short (60)	0 – 60	7.9	75	17	
8	6.40	Long (475)	0 – 130	34	42	NA	
			130 – 475		4	NA	
		Short (128)	0 – 128	36	35	41	76

DPV = Displaced Pore volume; NA = No Analysis

Table 3. Results of Aqueous-Phase Oxidation State Analyses.

pH	Sample	Oxidation State Distribution				
		III	IV	V	VI	0
3	long term spike	0	$7 \pm 1$	$90 \pm 5$	0	$6 \pm 1$
	short term spike	0	$4 \pm 1$	$78 \pm 5$	$14 \pm 2$	$5 \pm 1$
	short term effluent (1.9 – 2.4 DPV)	0	$1 \pm 1$	$83 \pm 5$	$9 \pm 1$	$7 \pm 1$
5	long term spike	$2 \pm 2$	$6 \pm 1$	$88 \pm 5$	$0 \pm 1$	$5 \pm 1$
	short term effluent (5.7 – 6.2 DPV)	0	$8 \pm 2$	$81 \pm 5$	$6 \pm 3$	$5 \pm 2$
8	long term spike	0	$3 \pm 1$	$89 \pm 4$	$2 \pm 1$	$8 \pm 1$
	short term spike	$7 \pm 2$	$14 \pm 2$	$71 \pm 5$	$3 \pm 2$	$5 \pm 1$
3	batch	NA	NA	$94 \pm 5$	NA	NA
5	batch	NA	NA	$91 \pm 5$	NA	NA
8	batch	NA	NA	$94 \pm 6$	NA	NA

NA = No analysis

The effluent data for the column tests show the presence of multiple Pu species, although the nature and origin of these species is open to speculation. Even though the system is relatively simple, there are a number of processes that could be important including colloidal transport, aqueous-phase speciation changes, and solid-phase speciation changes. Filtration ( $<0.02\text{-}\mu\text{m}$ ) analysis suggests that the multiple Pu peaks in the breakthrough curves were not attributable to

the presence of colloidal and non-colloidal phases. Because the oxidation state analyses showed the Pu in the first effluent peaks to be Pu(V) (at least for pH 3 and pH 5), it is likely that the first effluent peak is the  $\text{Pu(V)O}_2^+$  cation undergoing exchange reactions with the soil surface. The pH dependence of the position of this first breakthrough peak is consistent with classical cation sorption to metal oxide surfaces. Where, as observed in this study, increasing pH values result in a more negatively charged soil surface and, all other factors being equal, cation sorption increases due to stronger electrostatic interactions.

Due to detection limit constraints, no oxidation state analyses are available on the later low-activity peaks to discern their oxidation state distribution. As expected, the amount of Pu remaining in the soil after the major effluent peak increased as a function of increasing pH. For the pH 3 column tests, the solid-phase activity distribution (Figure 2B) exhibits a broad peak centered between 5 and 6 cm from the inlet which implies a retardation factor between 16 and 20 for the Pu (~10% of Pu spike) remaining in the column. This corresponds reasonably well with the small effluent peak at 24 displaced pore volumes observed in the long term test (the closed triangles in Figure 2A). At pH 5 (Figure 3B), the Pu was found distributed throughout the column, but approximately 30% of the activity was in the first two centimeters. At pH 8 (Figure 4B), over 60% was in the first two cm.

The nature of the Pu remaining in the soil is another unknown. Because formation constants for Pu(IV) surface species are extremely high (i.e., large  $K_d$  values), any mechanism that produces Pu(IV), either in solution or at the soil surface, would act to produce a less mobile Pu specie. This Pu(V) to Pu(IV) reduction mechanism is consistent with the data in this study at all pH values. Because no oxidation state analyses were conducted on the solid phase, considerable uncertainty exists as to potential surface mediated oxidation state changes in Pu during column transport. It has been reported, however, that iron and manganese (oxy) hydroxides like those present in the soils used for this study are capable of altering Pu oxidation state either by disproportionating Pu(V) into (IV) and (VI) or by surface mediated redox processes (Sanchez et al., 1985 and Duff et al., 1999). If this process is kinetically limited by the mass of Pu(V) sorbed to the surface as suggested by the Sanchez et al. work, then the extent of this reaction should be greatest under conditions of highest sorption (e.g., under higher pH conditions) and would be consistent with the development of a larger immobile fraction that was observed in this study.



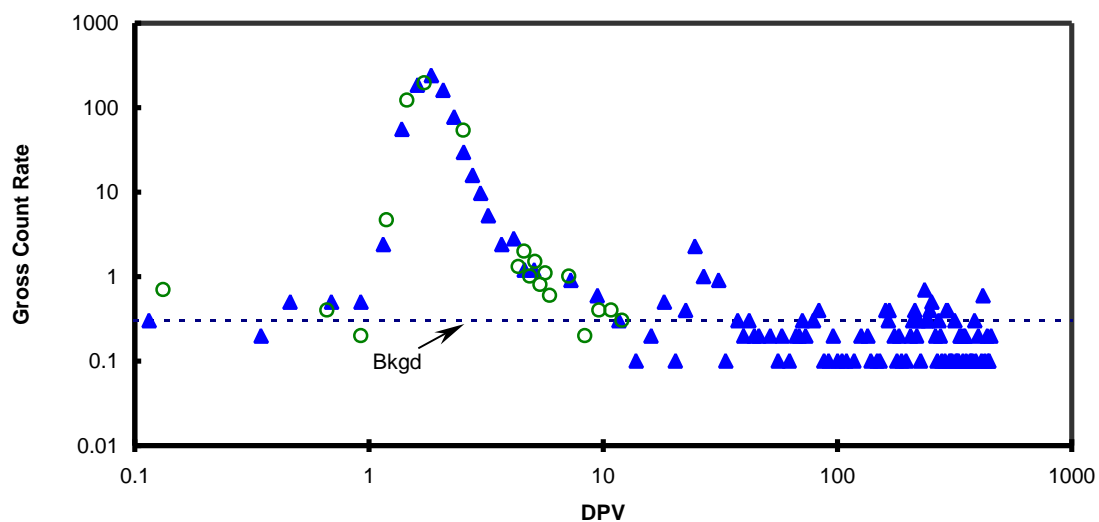


Figure 2A. Effluent Pu Activities pH 3 Column Tests: Circles = Short-Term Experiment, Triangles = Long-Term Experiment

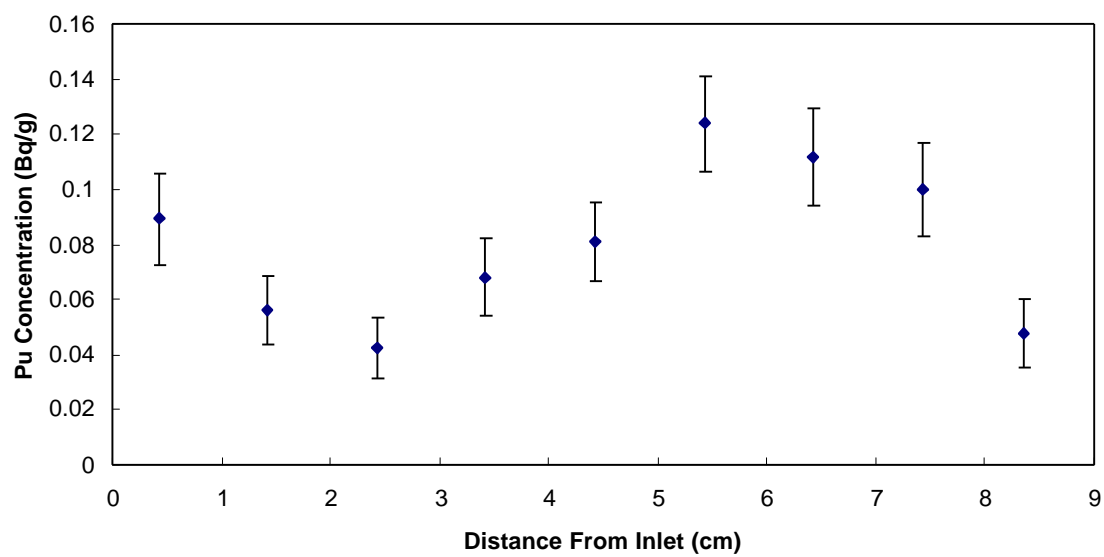


Figure 2B. Soil Pu Activities pH 3 at End of Short Column Test (circles in Figure 2A)

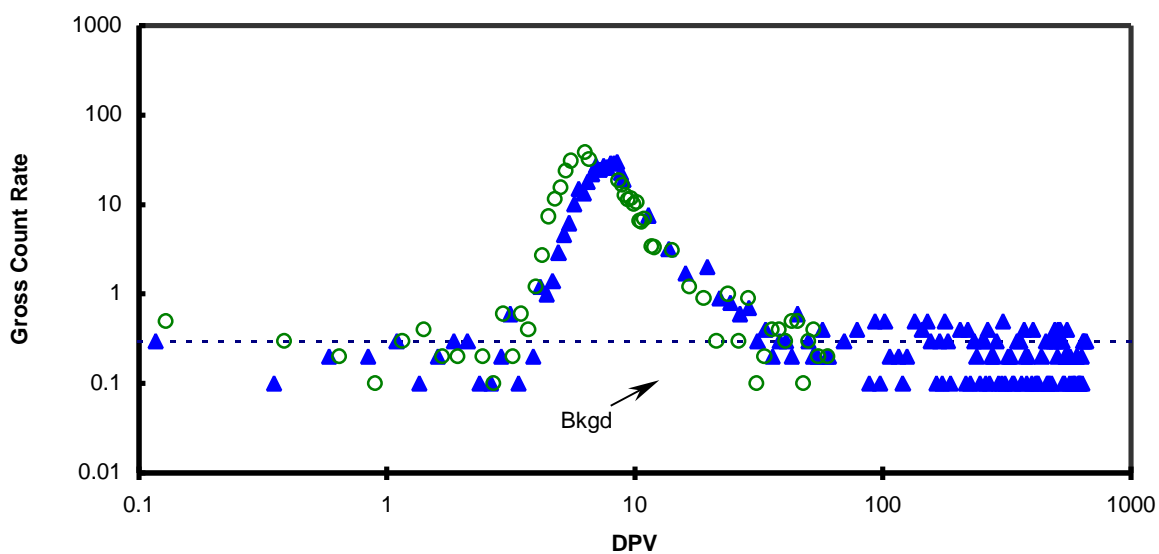


Figure 3A. Effluent Pu Activities pH 5 Column Tests: Circles = Short-Term Experiment, Triangles = Long-Term Experiment.

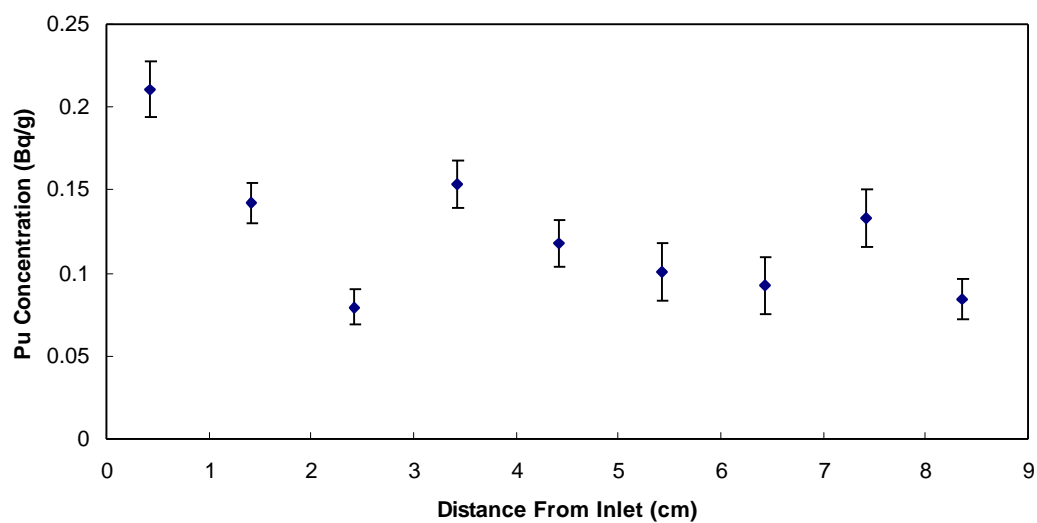


Figure 3B. Soil Pu Activities pH 5 at End of Short Column Test (circles in Figure 3A).

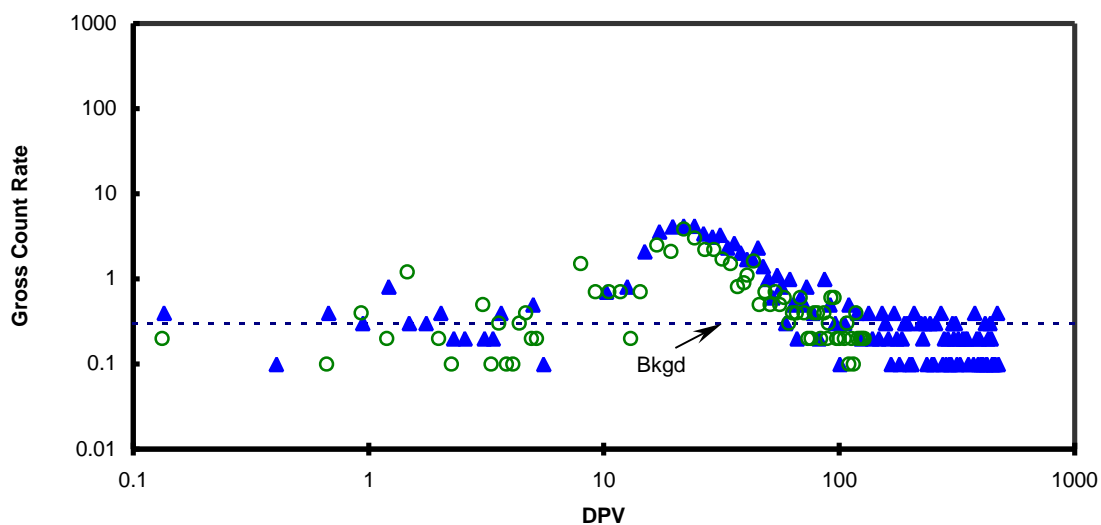


Figure 4A. Effluent Pu Activities pH 8 Column Tests: Circles = Short-Term Experiment, Triangles = Long-Term Experiment.

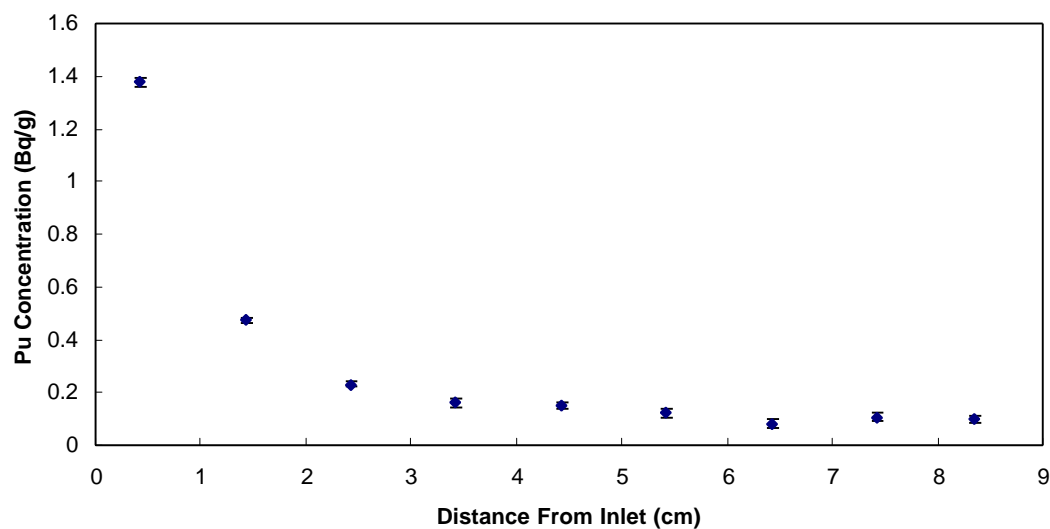


Figure 4B. Soil Pu Activities pH 8 at End of Short Column Test (circles in Figure 4A)

## 2.5 CONCLUSIONS

The results obtained here demonstrate that, even in a relatively simple system (i.e., very weakly binding ligands, low carbonate concentration, Pu(V) spike), multiple Pu species were present exhibiting a wide range of mobilities. At each pH, distinctly different mobile forms of Pu were observed. The breakthrough curves were all characterized by a well-defined peak, in which the average retardation factor and the fractional breakthrough varied with pH. At pH 3, there appeared to be both a “low” and “moderate” mobility fractions. At pH 5, there was a “moderate” mobility fraction that came through the column and the Pu remaining in the column showed a low mobility and was distributed over the entire column. At pH 8, about 35 % of the added Pu was recovered in the column effluent and this fraction exhibited a retardation factor of between 6 and 15 times that of the pH 3 and 5 data, respectively. The majority of the Pu remaining in the column for the pH 8 tests exhibited an extremely low mobility; however, there was a small but statistically significant fraction ( $<0.002$ ) of the total Pu that was transported through the columns with high mobility ( $1 < R < 2$ ). Although the flow velocities in the experiments were orders of magnitude higher than those typical of the subsurface, these results are consistent with the growing body of data showing multiple forms of Pu with distinctly different mobilities.

Data from this study are consistent with a mechanism where multiple forms of Pu are developed by a surface mediated reduction of Pu(V) to Pu(IV) by iron and manganese (oxy)hydroxides. If multiple forms of Pu are present under field conditions, transport models based on a single retardation factor derived from batch measurements of the distribution coefficient are clearly not appropriate and, alternately, more sophisticated models that can account for multiple species transport should be applied.

## 2.6 ACKNOWLEDGMENTS

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### **3.0 EVALUATION OF A CONCEPTUAL MODEL FOR THE SUBSURFACE TRANSPORT OF PLUTONIUM INVOLVING SURFACE MEDIATED REDUCTION OF Pu(V) AND Pu(IV)**

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#### **3.1 ABSTRACT**

A conceptual model is proposed to explain the transport behavior of plutonium in laboratory columns packed with a sandy coastal soil from the U. S Department of Energy's Savannah River Site. The column transport experiments, which are described elsewhere, involved the introduction of a finite step input of plutonium, predominately in the +5 oxidation state, into the columns and elution of the spike with a low-carbonate solution of 0.02 M NaClO<sub>4</sub> at pH 3, 5, and 8. Total plutonium concentrations were measured in the effluent as a function of time. These elution profiles suggest at least two distinct physical/chemical forms of plutonium, each with a different mobility. To explain the observed behavior, a conceptual model is proposed here which includes [1] equilibrium partitioning (both sorption and desorption) of plutonium (V) and plutonium (IV) between the aqueous and sorbed phases with pH-dependent, oxidation-state specific distribution coefficients and [2] kinetic reduction of plutonium (V) to plutonium (IV) in the sorbed phase. The conceptual model was applied to the column experiments through a one-dimensional advective/dispersive mathematical model, and predictions of the mathematical model were compared with the experimental data. Overall, the model provided excellent qualitative predictions of the major features observed in the experimental. It also yielded a quantitative estimate of the rate constant for surface mediated reduction of plutonium (V) to plutonium (IV) that was in the range of values reported in the literature for goethite mediated plutonium reduction.

#### **3.2 INTRODUCTION**

An implicit assumption in the classical models used for predicting contaminant transport in the subsurface is that the contaminant exists in a single physical/chemical form. The effect of interactions with the subsurface media on mobility is inferred from batch sorption experiments and is usually expressed through a single parameter, typically a distribution coefficient or the corresponding retardation factor. However, there is a growing body of field and laboratory data suggesting that this approach may not be appropriate for some contaminants, especially plutonium and other actinides. The field evidence comes from studies which find an unknown fraction of the contaminant inventory migrating much faster than predicted by the classical approach (Kaplan et al., 1994; Penrose et al., 1990; Buddenheimer and Hunt, 1998; Kersting et

al. 1999; McCarthy et al., 1998). This is supported by laboratory microscale and column experiments (Fried et al., 1974; Thompson, 1989; Fjeld et al. 2001; Serkiz et al., 2001) in which some contaminants exhibit behavior suggesting they can exist simultaneously in multiple physical/chemical forms with distinctly different mobilities.

Mechanisms such as colloidal generation and transport, formation of mobile complexes, and kinetic limitations have been advanced to explain these behaviors. It is likely that the mechanism for enhanced transport varies depending on the contaminant, the chemistry of the aqueous chemistry, and the physical/chemical characteristics of the solid phase. The column experiments reported by Serkiz et al. (2001) provide an opportunity to test a mechanistic model involving multiple forms of plutonium. In the experiments, a one pore volume spike of predominately plutonium (V) (with small amounts of plutonium (IV)) was introduced into a 1.5 x 8.7 cm column containing the 250 –420  $\mu\text{m}$  fraction of a sandy coastal plain soil from the U. S. Department of Energy's Savannah River Site. The column was eluted with low carbonate, 0.02 M  $\text{NaClO}_4$  solutions at pH 3, 5, and 8 for up to 650 pore volumes. Effluent plutonium concentrations (total plutonium) were measured as a function of time (expressed as number of displaced pore volumes) and the spatial distribution of plutonium in the soil was measured at the end of the elution period. The plutonium elution profiles were characterized by a large peak with a retardation factor that varied from 2 (for pH 3) to 30 (for pH 8). The peak contained between 90% (for pH 3) and 35% (for pH 8) of the plutonium in the input. Acid extractions of the soil in the column after the elution showed that most of the remaining plutonium could be accounted for in the solid phase. These depth discrete soil samples, in combination with the elution profiles, showed two "waves" of plutonium moving through the column, one with a relatively high mobility ( $R = 2$  to 30) and another with a lower mobility ( $R = 24$  to greater than 1000). Tritium was used as a conservative tracer in the experiments to provide hydrodynamic information, including dispersion coefficients. Dispersion coefficients were obtained through a least squares fitting option in the CXTFIT code (Parker and Van Genuchten, 1984). In these fits, the width of the finite step input and the mean linear velocity were specified, and the dispersion coefficient was the fitting parameter. For the six columns, the fitted dispersion coefficient was  $0.030 \pm 0.0008 \text{ cm}^2/\text{s}$ .

Presented in this paper is a conceptual model for plutonium (IV and V) transport in the soil/eluent system employed in the above-described experiments. The model is applied to the experimental column geometry through a one-dimensional advective/dispersive mathematical model, and the effect of the transport parameters on predicted plutonium elution profiles and spatial distributions in the soil are illustrated for hypothetical sets of parameter values. The model is evaluated through comparisons with the experimental data.

### 3.3 METHODS

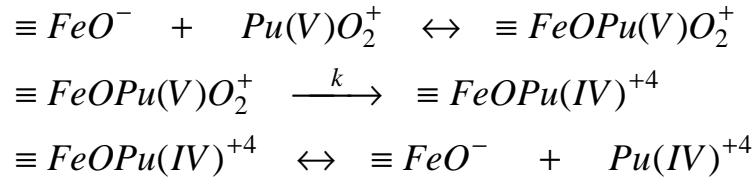
#### 3.3.1 Mathematical Model

To explain the transport behavior of plutonium in the experiments described above, a conceptual model is proposed which accounts for two aspects of the environmental chemistry of plutonium. The first is that the predominant form of plutonium in natural waters is plutonium (V) (Choppin



and Stout, 1989). The second is that the reduction of actinide (V) to actinide (IV) is possible through surface mediated reactions (Sanchez et al., 1985; Keeney-Kennicutt and Morse, 1985). These factors suggest a conceptual model involving equilibrium partitioning of plutonium (V) between the aqueous and solid phases, surface mediated kinetic reduction of some of the sorbed plutonium (V) to plutonium (IV), and the subsequent equilibrium partitioning of plutonium (IV) between the aqueous and solid phases.

The reactions can be expressed symbolically as follows:



where  $\equiv FeO^-$  is an iron surface binding site on the solid and k is the first-order rate constant for surface mediated reduction of plutonium (V) to plutonium (IV).

Incorporating kinetic reduction of solid phase plutonium (V) to plutonium (IV) into the one-dimensional advection/dispersion equation yields the following coupled equations:

$$\frac{\partial C_v}{\partial t} + \frac{r \partial S_v}{n \partial t} = D \frac{\partial^2 C_v}{\partial x^2} - v \frac{\partial C_v}{\partial x} - \frac{k r S_v}{n} \quad (1)$$

$$\frac{\partial C_{IV}}{\partial t} + \frac{r \partial S_{IV}}{n \partial t} = D \frac{\partial^2 C_{IV}}{\partial x^2} - v \frac{\partial C_{IV}}{\partial x} + \frac{k r S_v}{n} \quad (2)$$

where V refers to plutonium (V), IV refers to plutonium (IV) and where C is aqueous phase plutonium concentration (Bq/mL), S is solid phase plutonium concentration (Bq/g), D is dispersion coefficient (cm<sup>2</sup>/s), v is mean linear velocity (cm/s), k is the first-order rate constant for solid phase reduction of plutonium (V) to plutonium (IV) (/s), ρ is bulk soil density (g/cm<sup>3</sup>), and n is porosity. The solid phase reduction of plutonium (V) to plutonium (IV) is represented by the third term on the right hand side of Eqs. 1 and 2.

The equations can be simplified by approximating the solid/liquid phase partitioning of plutonium (IV) and plutonium (V) as a linear, instantaneous, reversible process through pH-dependent, oxidation state specific distribution coefficients. This yields

$$R_v \frac{\partial C_v}{\partial t} = D \frac{\partial^2 C_v}{\partial x^2} - v \frac{\partial C_v}{\partial x} - k' C_v \quad (3)$$

$$R_{IV} \frac{\partial C_{IV}}{\partial t} = D \frac{\partial^2 C_{IV}}{\partial x^2} - v \frac{\partial C_{IV}}{\partial x} + k' C_v \quad (4)$$

where

$$R_v = 1 + \frac{r K_D^v}{n} \quad (5)$$

$$R_{IV} = 1 + \frac{rK_D^{IV}}{n} \quad (6)$$

$$S_V = K_D^V C_V \quad (7)$$

and

$$k' = \frac{k r K_D^V}{n} \quad (8)$$

McGinnis (2000) obtained analytical solutions for the advective versions (i.e.  $D = 0$ ) of equations of Eqs. 3 and 4 by Laplace Transforms. To facilitate comparisons with the column data, the equations were solved here by a fully implicit, second-order finite difference method for the following boundary conditions:

$$C_V(0,t) = \begin{cases} \alpha C_0 & 0 \leq t \leq T \\ 0 & t > T \end{cases} \quad \frac{\partial C_V(L+\Delta x)}{\partial x} = \frac{\partial C_V(L-\Delta x)}{\partial x} \quad (9)$$

$$C_{IV}(0,t) = \begin{cases} (1-\alpha)C_0 & 0 \leq t \leq T \\ 0 & t > T \end{cases} \quad \frac{\partial C_{IV}(L+\Delta x)}{\partial x} = \frac{\partial C_{IV}(L-\Delta x)}{\partial x} \quad (10)$$

where  $T$  is the width of the finite step spike,  $C_0$  is total plutonium concentration in the spike,  $\alpha$  is the plutonium (V) fraction in the spike,  $L$  is the length of the column, and  $\Delta x$  is the length of one block in the finite difference grid.

### 3.3.2 Transport Parameters

The key transport parameters are the two retardation factors,  $R_{IV}$  and  $R_V$ , and the reduction rate constant,  $k$ . Near-surface soils from the Savannah River Site are typified by sand and kaolinite soil grains with iron (oxy)hydroxides (e.g. hydrous ferric oxide (HFO) and goethite) (Johnson, 1995). Data for the sorption of both plutonium (IV) and plutonium (V) to goethite and reduction of plutonium (V) to plutonium (IV) by goethite from Sanchez et al. (1985) were used to represent the surface chemistry of plutonium in our model. However, Sanchez et al. (1985) conducted sorption experiments with the pure ferric oxide mineral phase, goethite, for both plutonium (IV) and plutonium (V). Sanchez et al. conducted experiments for equilibration times of 1 hour, 24 hours, 60 hours, 96 hours, 5 days, and 30 days. With increasing equilibration time, the sorption edge shifted from higher pH values to lower pH values. The one-hour data (as reported by Turner (1995)) were used here because the residence time in the column experiments being modeled was on the order of minutes. Distribution coefficients for plutonium (IV) and plutonium (V) to goethite were calculated at each pH. To apply these distribution coefficients, which are for the pure mineral phase, to the soil used in the column experiments, an extrapolation based on specific surface area was used, i.e.,

$$K_D^{COL} = \frac{y^{COL}}{y^{PM}} K_D^{PM} \quad (11)$$

where  $\psi$  is specific surface area ( $\text{m}^2/\text{g}$ ), COL refers to the soil in the column experiments, and PM refers to the pure mineral phase. Specific surface area of the soil used in the column experiments was not available. However, an upper bound estimate was made using Johnson's (1985) empirical relation for the total soil, i.e.,

$$y^{SRS} = 51f_{\text{clay}} + 0.68 \quad (12)$$

where  $f_{\text{clay}}$  is the clay fraction for the soil. Based on a clay fraction of 0.039, the specific surface area was  $2.67 \text{ m}^2/\text{g}$ . Because the iron oxide found in the SRS soil is amorphous, the specific surface area of hydrous iron oxide was considered to be more appropriate than that for goethite, which is crystalline. A value of  $600 \text{ m}^2/\text{g}$  (Dzombak and Morel, 1990) was used in the calculations. Retardation factors were then calculated from

$$R = 1 + \frac{\rho K_D}{n} \quad (13)$$

where  $\rho$  ( $1.64 \text{ g/cm}^3$ ) and  $n$  (0.32) are column bulk soil density and porosity, respectively.

Although the column experiments were conducted with influent pH values of 3, 5, and 8, the buffering capacity of the study soils had the effect of altering the effluent pH. The pH 3 influent increased to approximately 3.5, the pH 5 decreased to approximately 4.75, and the pH 8 influent decreased to approximately 4.9. For modeling purposes, retardation factors corresponding to the mean pH (i.e. approximately half way between the influent pH and the effluent pH) were specified. The pH values and resultant retardation factors are given in Table 1.

Table 1. Retardation Factors Based on Sorption Data from Sanchez et al. (1985)

Influent pH	Mean effluent pH	$R_{IV}^a$ at mean pH	$R_V^a$ at mean pH
3	3.25	35	$1.29^c$
5	4.9	1500	6.1
8	6.4	7900	24

<sup>a</sup>  $R_{IV}$  = retardation factor of plutonium (IV) (Equation 6).

<sup>b</sup>  $R_V$  = retardation factor of plutonium (V) (Equation 5).

<sup>c</sup>  $R_V$  at pH 3.76, which is the lowest pH in the data set.

Sanchez et al. (1985) and Keeney-Kennicutt and Morse (1985) report kinetic data on the solid phase reduction of plutonium (V) to plutonium (IV) by iron oxides. Keeney-Kennicutt and Morse measured the relative proportions of plutonium (IV), (V), and (VI) in the solid phase as a function of time. McGinnis (2000) used their data on the decrease in plutonium (V) to estimate a first-order reduction rate constant for plutonium (V) to plutonium (IV) and obtained values ranging from  $10^{-3} \text{ /s}$  to  $10^{-7} \text{ /s}$ . Sanchez et al. measured the increase of plutonium (IV) in the

solid phase with time. From these data, McGinnis (2000) estimated reduction rate constants for the same system in the range from  $10^{-4}$  to  $10^{-5}$  /s.

### 3.4 RESULTS

#### 3.4.1 Predicted Plutonium Transport Behavior

Presented here are model predictions of plutonium concentrations in the effluent of one-dimensional columns as a function of time, expressed as the number of displaced pore volumes. The objective is to illustrate the effect of the key transport parameters,  $R_{IV}$ ,  $R_V$ , and  $k$ , on elution profiles. To facilitate qualitative comparisons with the experimental results of Serkiz et al., total plutonium is shown in addition to plutonium (IV) and plutonium (V).

The effect of reduction rate constant on plutonium transport is illustrated in Fig. 1, where elution profiles are shown for  $R_{IV} = 10$ ,  $R_V = 2$ , and a range of plutonium reduction rate constants. For  $k = 10^{-5}$  /s (Fig. 1a), the elution profile is characterized by a single peak at 2 DPV, due solely to plutonium (V). This occurs because reduction is too slow for there to be a significant production of plutonium (IV) during the time it takes for plutonium (V) to traverse the column. For  $k = 10^{-1}$  /s (Fig. 1c), the elution profile is characterized by a single peak of predominately plutonium (IV) at 10 DPV. This occurs because the reduction rate is so rapid that essentially all of the plutonium (V) entering the column is quickly reduced to plutonium (IV) which then is transported more slowly through the column. For  $k = 10^{-3}$  /s (Fig. 1b), there are two peaks in the elution profile. The peak at 2 DPV is fairly distinct and is due primarily to plutonium (V). Oxidation state analysis of eluate from a peak at approximately this same location in the column experiments (Serkiz et al., 2001) was consistent with this model prediction [83% plutonium (V) and 9% plutonium (IV)]. The second peak extends from 2 to 10 DPV and is due primarily to plutonium (IV) which is produced by the continuous reduction of plutonium (V) and subsequently migrates through the column. As the reduction rate increases, the relative importance of the peak at 2 DPV (corresponding to plutonium (V)) decreases relative to the peak at 10 DPV (due to plutonium (IV)).

The effect of the plutonium (IV) retardation factor ( $R_{IV}$ ) is illustrated in Fig. 2, where elution profiles are given for  $R_V = 2$ ,  $k = 10^{-3}$  /s, and  $R_{IV} = 10$  (Fig. 2a), 30 (Fig. 2b), and 100 (Fig. 2c). These profiles are characterized by a plutonium (V) peak at 2 DPV and a plutonium (IV) continuum extending to 10, 330, and 100 DPV. The continuum is due to the continuous production of plutonium (IV) (and its subsequent migration through the column) on the solid phase as plutonium (V) migrates through the column.

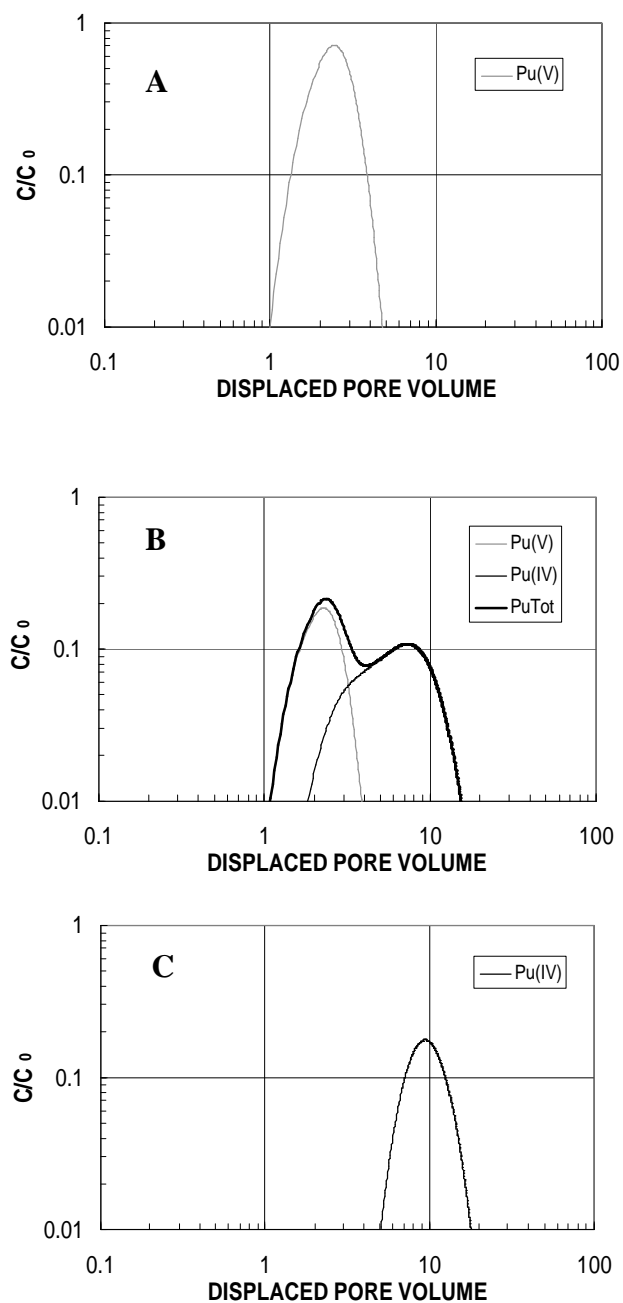


Figure 1. Predicted effluent profiles for  $R_v = 2$  and  $R_{IV} = 10$  and A)  $k=10^{-5} \text{ s}^{-1}$ ; B)  $k=10^{-3} \text{ s}^{-1}$ ; C)  $k=10^{-1} \text{ s}^{-1}$ . The following values were used in all of the predictions:  $v = 0.008 \text{ cm/s}$ ,  $D = 0.0030 \text{ cm}^2/\text{s}$ , and  $L = 8.7 \text{ cm}$ .

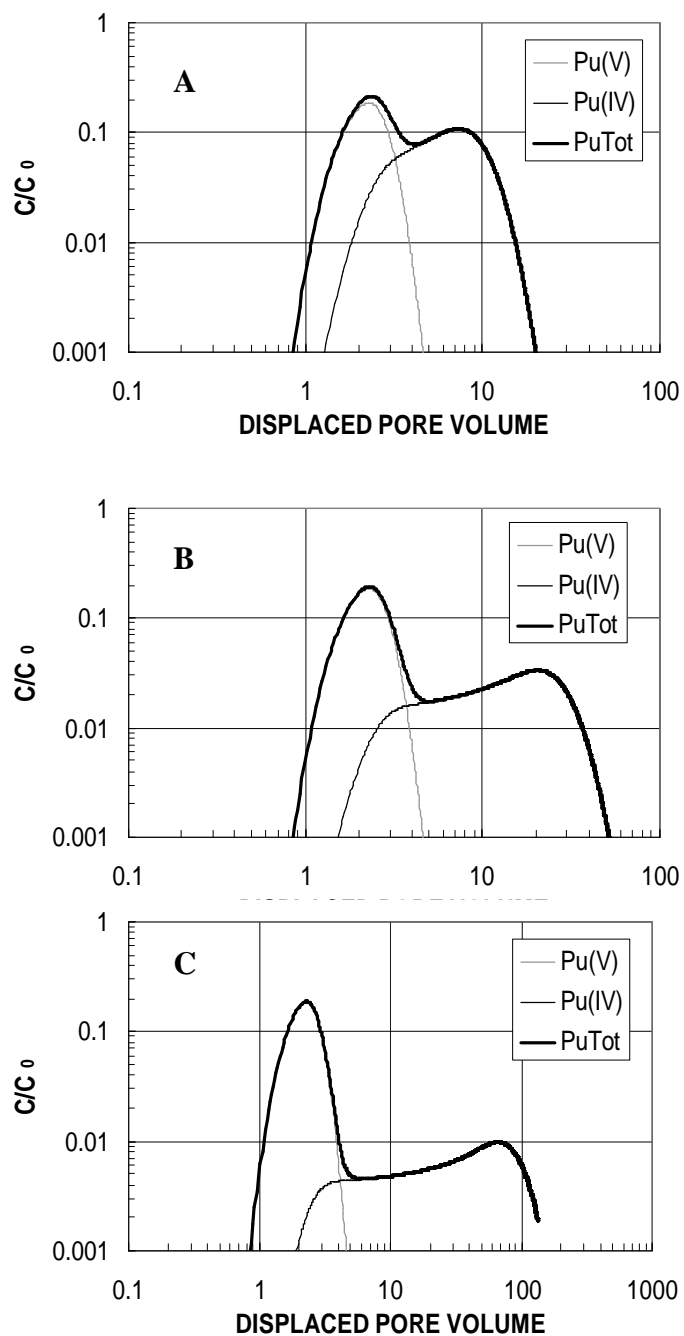


Figure 2. Predicted effluent profiles for  $R_V = 2$ : A)  $k = 10^{-3}$  /s and  $R_{IV} = 10$ ; B)  $R_{IV} = 30$ ; and C)  $R_{IV} = 100$ .

### 3.4.2 Comparisons of Predictions with Experiment

Model predictions for total plutonium are compared to the experimental data in Fig. 3. Calculations were performed for  $k = 10^{-3}$  /s and  $k = 10^{-5}$  /s and the retardation factors in Table 1. For  $k = 10^{-5}$  /s, the agreement is reasonable at all three pHs in that the predicted peak locations match up well with the data. For  $k = 10^{-3}$  /s, agreement is good at pH 3 and poor at pH 5 and 8. Although the comparisons for  $k = 10^{-5}$  /s provide a degree of validation of the plutonium (V) retardation factors in Table 1, they do not provide any insight into validity of the surface reduction component of the model, which affects the fractional recovery. Predicted fractional recoveries for  $k = 10^{-3}$  /s and  $k = 10^{-5}$  /s are compared to those from the experiment in Table 2. At pH 3, the predicted recovery is essentially unity for both rate constants and the experimental recovery is 0.9. For pH 5 and 8, the experimental recoveries lie between those for  $k = 10^{-3}$  /s and  $10^{-5}$  /s.

Table 2. Comparison of Experimental and Theoretical Fractional Recoveries

pH	Experiment	Theory	
		$k = 10^{-3}$ /s	$k = 10^{-5}$ /s
3	0.9 (col 1)	0.99	1.0
	0.9 (col 2)		
5	0.74 (col 1)	0.00	0.95
	0.75 (col 2)		
8	0.42 (col 1)	0.00	0.72
	0.35 (col 2)		

Table 3. Fitted Values of k

pH	Experimental Fractional Recovery of Plutonium	Fitted Reduction Rate Constant
pH 3	0.9 (col 1)	$2 \times 10^{-4}$ /s
pH 5	0.74 (col 1)	$3 \times 10^{-5}$ /s
pH 8	0.42 (col 1)	$1.3 \times 10^{-5}$ /s

The predicted dependence of fractional recovery on reduction rate constant suggested an alternative means of evaluating the model. Graphs of fractional recovery as a function of rate constant were generated for each pH. From these graphs, fitted values of k were obtained (Table 3). The best fit reduction rate constants varied from  $2 \times 10^{-5}$  to  $2 \times 10^{-4}$  /s (3) depending on pH and were all in the range of rate constants inferred from the data of Sanchez et al (1995).

One feature of the experimental data that is not predicted by the model is the small peak at 30 DPV for pH 3. One explanation for this is that it is due to a small amount of plutonium (IV) in the spike (Serkiz et al., 2001). This explanation is plausible given that the spike was typically 90

– 95% plutonium (V) and 3 to 14% plutonium (IV). Thus, calculations were performed for a spike containing 90% plutonium (V) and 10% plutonium (IV). The calculations used the fitted values of  $k$  and the experimental retardation factors. Elution profiles based on the predictions are compared with the experimental data in Fig. 4. At pH 3 (Fig. 4a), the model captures both of the peaks observed in the experiment. At pH 5 and 8, the model predictions are qualitatively consistent with the data in that they predict a slightly elevated (i.e. above background) response following the passage of the main peak. However, the predicted magnitude of this response is smaller than that observed in the experiments.

Predictions of soil concentrations are compared with the data in Fig 5. The agreement between the experimental data and the predictions were not as good as for the elution profiles. For example, at pH 5 (Fig. 5b) the model predicts a large peak in the first two centimeters of the column which were not seen in the data, and at pH 3 (Fig 5a) the model predicts a very low concentration near the inlet whereas it was slightly elevated in the experiments. Nonetheless, the model captured two major features observed in the data. At pH 3, the data show a peak at a distance of 5 – 7 centimeters from the inlet, and the model predicts a peak around 4 cm. At pH 8 (Fig. 5c), the data show most of the plutonium within 2 cm of the inlet, and the model predicts the same.



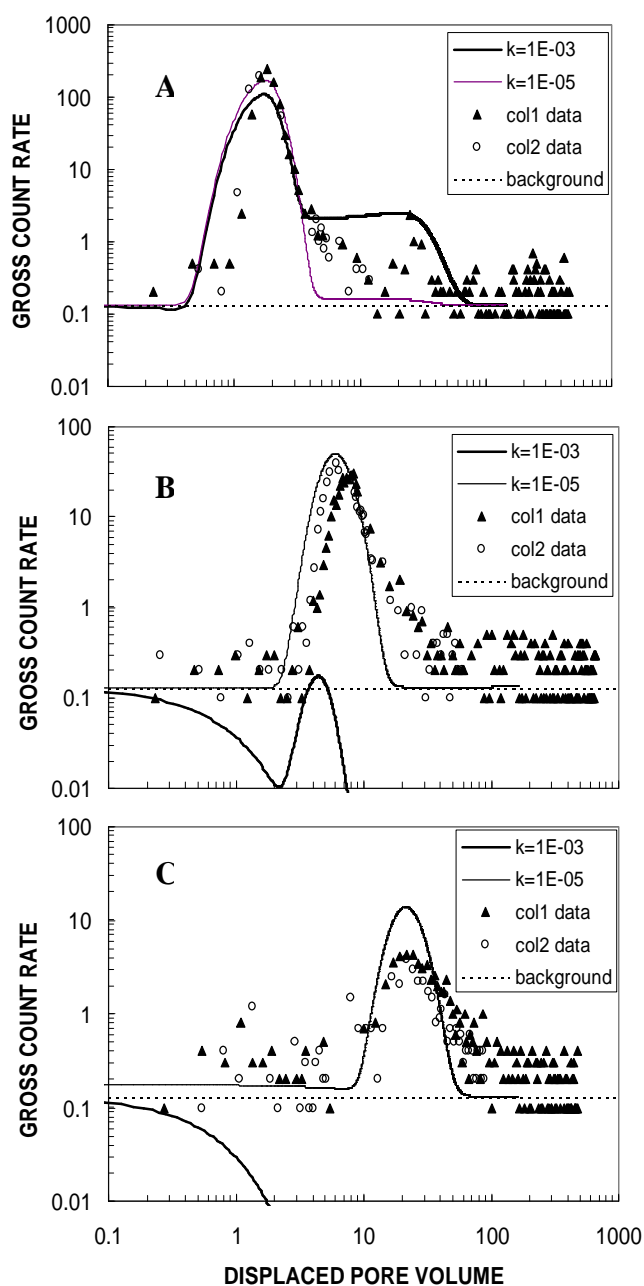


Figure 3. Comparison of model predictions of total plutonium with experimental data based on retardation factors from Table 2 and  $k = 10^{-5}$  /s and  $k = 10^{-3}$  /s: .A) pH=3,  $R_V=1.29$ ,  $R_{IV}=35$ ; B) pH=5,  $R_V=6.1$ ,  $R_{IV}=1500$ ; and C) pH=8,  $R_V=24$ ,  $R_{IV}=7900$ .

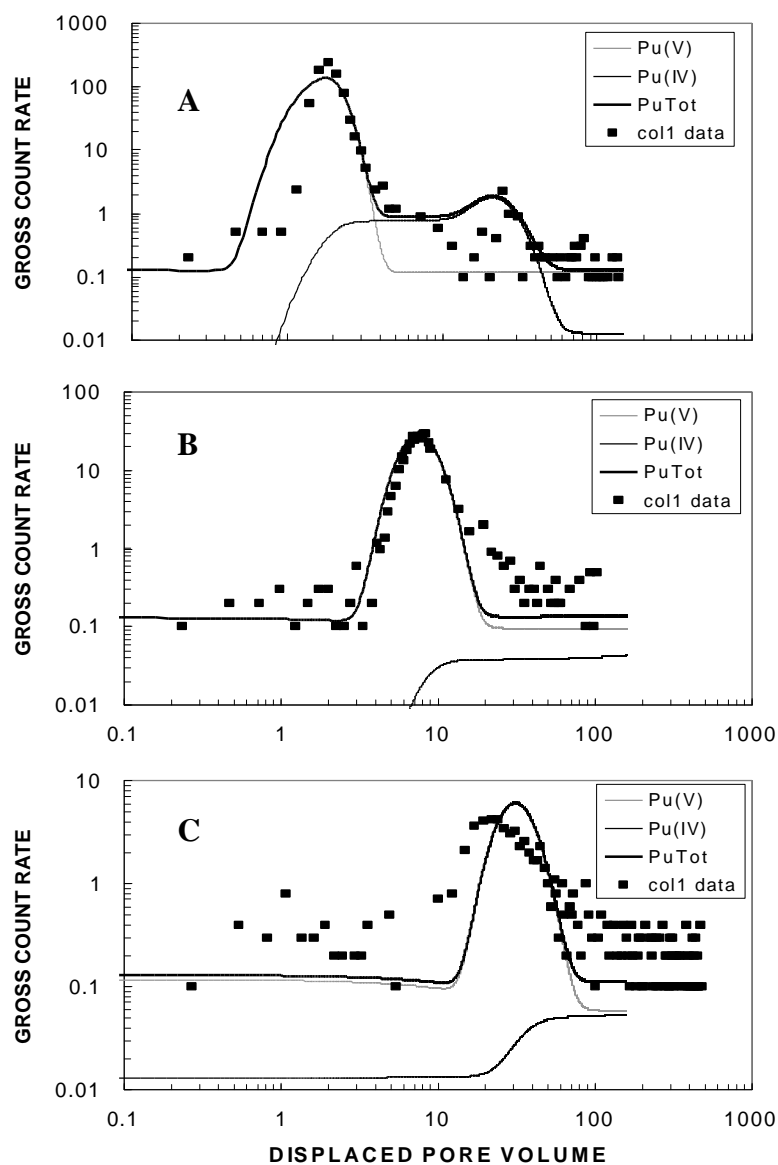


Figure 4. Comparison of predicted elution profile with with experimental data for a spike containing 90% plutonium (V) and 10% plutonium (IV) using the fitted reduction rate constant and the experimental retardation factors. A) pH = 3,  $k = 2 \times 10^{-4}$  /s,  $R_{IV} = 25$ , and  $R_V = 1.3$ . B) pH = 5,  $k = 3 \times 10^{-5}$  /s,  $R_{IV} = 1200$ , and  $R_V = 7.9$ . C) pH = 8,  $k = 1 \times 10^{-5}$  /s,  $R_{IV} = 2600$ , and  $R_V = 36$ .

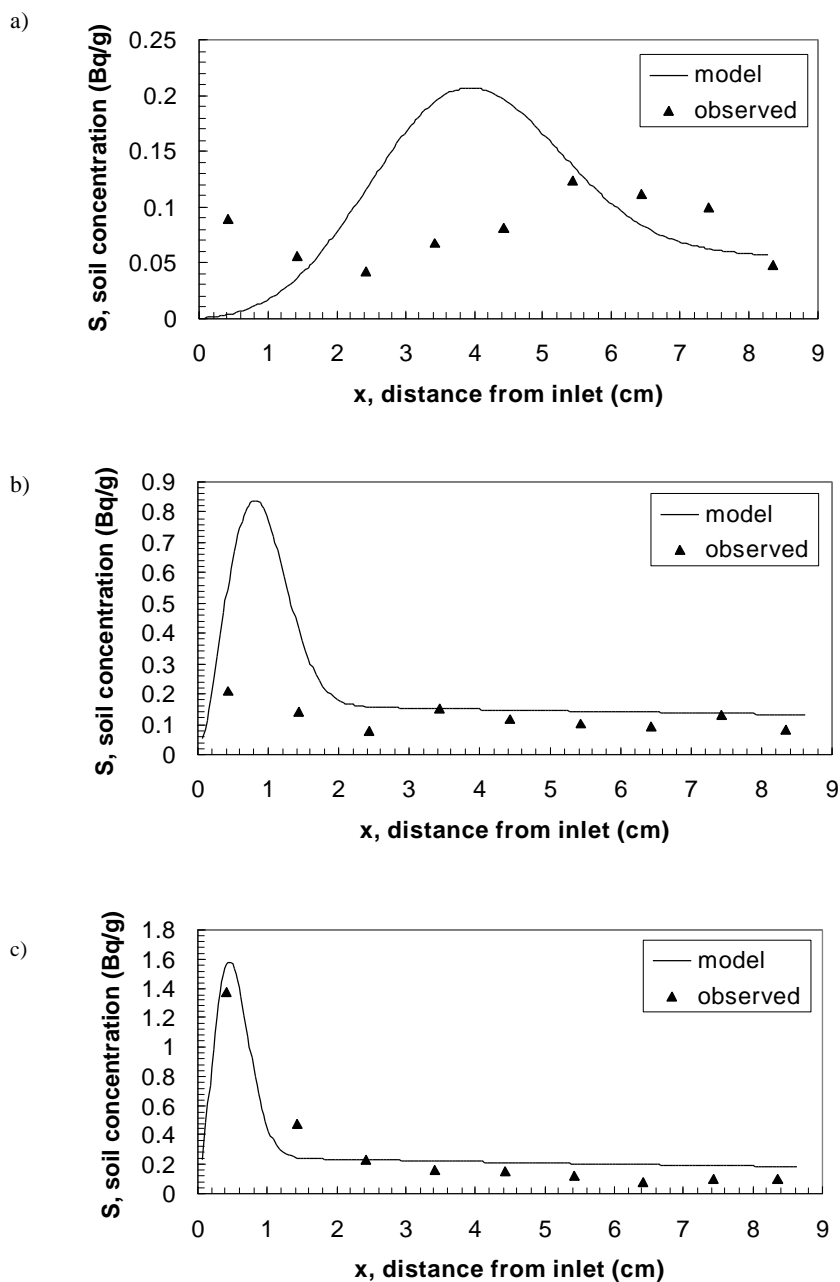


Figure 5. Comparison of predicted soil spatial distribution with experiment data for a spike containing 90% plutonium (V) and 10% plutonium (IV) with experimentally derived values of the transport parameters: a) pH = 3,  $k = 2 \times 10^{-4}$  /s,  $R_{IV} = 25$ , and  $R_V = 1.3$ ; b) pH = 5,  $k = 3 \times 10^{-5}$  /s,  $R_{IV} = 1200$ , and  $R_V = 7.9$ ; and c) pH = 8,  $k = 1 \times 10^{-5}$  /s,  $R_{IV} = 2600$ , and  $R_V = 36$ .

### 3.5 CONCLUSIONS

In the column experiments described by Serkiz et al. (2001), plutonium transport in a sandy coastal plain soil was characterized by three major features: (1) the presence of two plutonium species with distinctly different mobilities, (2) a decrease in mobility with increasing pH for both species, and (3) a decrease in fractional recovery with increasing pH for the more mobile species. The model proposed here, which includes [1] equilibrium partitioning of plutonium (V) and plutonium (IV) between the aqueous and sorbed phases with pH-dependent, oxidation state specific distribution coefficients and [2] kinetic reduction of plutonium (V) to plutonium (IV) in the sorbed phase, shows both qualitative and quantitative agreement with the experimental data. The multiple species observed in the experiments are consistent with surface mediated reduction of plutonium (V) to plutonium (IV). The experimentally observed decrease in mobility with increasing pH is qualitatively consistent with sorption data from the literature for plutonium (IV and V) on goethite. In addition, the magnitudes of the retardation factors inferred from the literature data are in good agreement with those observed experimentally. However, this agreement must be viewed with caution as the value inferred from the literature is based on an upper bound estimate of the specific surface area of the soil in the column experiments. Finally, the decrease in fractional recovery of plutonium (V) observed in the experiments is predicted by the model, and best fit values of the reduction rate constant are in the range of values reported in the literature.

### 3.6 ACKNOWLEDGMENTS

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